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COMPLETE SPECIFICATION

NO DRAWINGS

Process for Preparing High Molecular Homo-polymerizates and Co-polymerizates of Alpha-Methyl-Styrene

We, RÜTGERSWERKE UND TEERVERWERTUNG AKTIENGESELLSCHAFT of Mainzer Landstrasse 195-217, 6000 Frankfurt am Main 1, Germany, a German Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

It has been known that α-methylstyrene can be polymerized to high-molecular products with the aid f alkali metals, if polymerization is carried out in the presence of ethers, acetals, and particularly in the presence of cyclic ethers, such as tetrahydrofuran or dioxane. Instead of alkali metals, alkali hydrides can also be used. In the polymerization of polymerizable monomers alone or together with monomers capable of mixed polymerisations, such as, for example, vinylsubstituted aromatic hydrocarbons, lithium-organic compounds can also be used as catalysts. Thereby, the solvent used has also a certain influence on the velocity of polymerization and on the structure of the resulting polymers. While in polymerization in non-polar solvents, for long polymerization times low-molecular products are obtained, in the presence of a polar solvent, such as tetrahydrofuran, an increase of the reaction velocity can be attained.

This invention consists in a process for preparing homopolymerizates of α-methylstyrene and copolymerizates of α-methylstyrene with other ethylenically unsaturated monomers characterized in that the polymerization is carried out in the presence of both organometallic compounds of lithium, in the range of 3 to 20 milli mols per mol of monomer, and a polymerization accelerator comprising a polyglycol of the formula

$$HOCH_2(—CH_2—O—CH_2)_n CH_2OH$$

wherein n has a value of from 5 to 200, the accelerator being present in an amount of from 0.5 to 2.0%, calculated on the weight of the monomers to be polymerized and the polymerization is carried out at a temperature of from −60° to +60°C.

In comparison to processes, in which polar solvents, such at tetrahydrofuran, are used, according to the present invention with essentially smaller amounts of the polymerization accelerator and in shorter reaction times, products can be obtained, the K-valve and softening points of which are more favourable for processing the resulting polymerizates. Polymerisation can be carried out continuously, as well as discontinuously. By using suitable devices, such as kneading machines or worms, and also by proceeding in dilute solution, uniform reaction, satisfactory intermixing and removal of heat, can be attained. Oxygen, water and alcohols, must be carefully excluded. It is preferred to carry out polymerization under pure nitrogen or argon.

The preferred solvents are aromatic hydrocarbons, such as benzene, toluene, xylene and cumene and also aliphatic hydrocarbons, such as heptane and isoctane. Polymerization can be carried out also in the absence of solvents. However, it may happen that, depending on the amount of the catalyst and co-catalyst, polymerization takes place very quickly, so that it may become difficult to remove the reaction heat.

As catalysts, organo-lithium compounds, for example isopropyl-lithium, n-butyl-lithium, sec.-butyl-lithium, octyl-lithium or phenyl-lithium, are used. Usually, solutions in hexane or heptane, containing 10-20% of the organo-lithium compounds are used. The quantity of catalyst used is influenced by the degree of purity of the solvent and of the monomers.

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The polyglycols used in the invention can be etherified with alipatic monohydric or polyhydric alcohols or aninoalcohols, or they can be esterified with organic acids, for example, polyhydroxyethylene cetylether, polyhydroxyethylene laurylether, polyhydroxyethylene sorbitan monolaurate, polyhydroxyethylene sterate, hydroxyalkylated triethanolamine and polyethyleneglycol dioleate. These substances can be used by themselves, or in mixture with each other, or in mixture with hydroxyalkylated phenols, by using various accelerators, products having desired K-values can be obtained.

α-methylstyrene can be polymerized by itself or together with other monomers. In dependence on the polymerization parameters or the monomers, the latter are introduced into the reaction either as a mixture, or in the sequence of the polymerization velocities of the monomers. For example, the following compounds can be used: styrene, vinylpyridine, 1-isopropyl-4- isopropenylbenzene, methylmethacrylate, acrylonitrile, methylpentadiene and butadiene. The monomers should be well purified, and they are preferably polymerized directly after their distillation. It is of particular interest that by means of the co-catalysts according to the invention improved mixed polymerizates of α-methylstyrene and styrene can be obtained in short reaction times, with simple processing of the reaction mixtures and in good yields. This is true in the case of mixed polymerizates containing a high proportion of styrene, as well as mixed polymerizates with a high proportion of α-methylstyrene. Mixed polymerizates containing a high proportion of styrene, are distinguished by high resistance to heat, while at high proportions of α-methyl styrene, lower softening points are attained, whereby processing of the polymerizates is facilitated. A pure poly-α methylstyrene has a high softening point and at the necessary injection temperature a certain depolymerization may occur.

Polymerisation is carried out at temperatures in the range between −60° and +60° C. Polymerisates and mixed polymerisates having particularly satisfactory characteristics can be obtained with particularly good yields if polymerization is started at temperatures above +10° C and is completed at a desired temperature below +10° C, for example, −60° C.

In carrying out polymerization, selectively two procedures can be used.

According to one of these procedures, the solvent, accelerator, and catalyst are introduced into the reaction vessel and then a small amount of the monomer (or monomers) is added at about +15° C. After the formation of a colored complex—within a few seconds up to about 3 minutes—the reaction vessel is cooled to the desired reaction temperature. During this cooling period, the monomer, or monomer mixture, is further slowly added drop by drop.

According to the second procedure, the total amount of the monomer, or monomer mixture, including the solvent and the accelerator, are introduced into the reaction vessel, the catalyst is added at about 15° C and after formation of the coloured complex cooling to the desired reaction temperature is effected.

At a later point of time, i.e. at a correspondingly lower temperature, further monomers can be added. The reaction solution slowly becomes more viscous during the cooling period. The average reaction time is in the range of 1.5 to 4 hours. After this reaction time, the product is precipitated from methanol, to which some acetic acid has been added. The product is washed with methanol and dried in vacuum at 100 to 120° C. The yields are in the range of 60 to 90%. The K-values are determined according to Fikentscher (Cellulosechemie *13* (1932) 58) in a 1% solution of the polyermizate in toluene. The softening points were determined on the Kofler heating bank, (see Mikrochemise, Vol 34 (1949/50) pages 374-381).

Example 1

In a reaction vessel provided with a stirrer, under nitrogen 100 g of α-methylstyrene, 50 g of toluene, and 1 g of polyhydroxy-ethylene stearate are mixed and at 15° C 0.5 g of butyllithium (15% solution inhexane) are added. The reaction starts with strong discoloration of the solution and the temperature rises to about 30° C. After 5 minutes reaction time, again 0.1 g of butyllithium and 50 g of toluene are added. After 1 hour the viscous reaction solution is diluted with benzene and the polymer is precipitated from methanol, to which some acetic acid is added. The product is dried at 100° C in vacuum.

Softening point:
196° C

K-value: 45.42

Example 2

Into a mixture consisting of 100 g of α-methylstyrene, 50 g of toluene, 0.5 g of hydroxyethylated β-naphthol and 0.5 g of polyhydroxyethylene - cetylether, at 20° C under nitrogen 0.5 g of n-butyllithium (15% solution in hexane) are injected. After reaction times of 5 and 10 minutes, at each time 0.15 g of butyllithium and 50 g of toluene, are added. After 1 hour, the reaction solution is diluted with benzene and the polymer is precipitated from methanol, to which some acetic acid is added. The polymer is dried at 120° C in vacuum.

Softening point:
195° C

K-value: 56.2

Example 3

In a nitrogen atmosphere, to a mixture of 50 g of α-methylstyrene, 50 g of toluene and 1 g of polyhydroxyethylene-cetylether, at 10° C 0.5 g of n-butyllithium (15% solution in hexane) are added. After 20 minutes reaction time, 50 g of styrene dissolved in 200 g of toluene are added drop by drop in quick succession. As the reaction solution becomes very viscous upon the addition of styrene, during this time, toluene is added twice, each time in an amount of 150 g. Simultaneously with each addition of toluene, 0.1 g of n-butyllithium or sec.-butyllithium is added. After a total reaction time of 1 hour and 20 minutes, the reaction solution is diluted with benzene and the polymer is precipitated in methylalcohol, to which some acetic acid is added. The polymer is dried in vacuum at 100° C.
Softening point:
150° C

K-value: 58.24

Composition of the polymer:

51.5% styrene
48.5% α-methylstyrene

Example 4

In a nitrogen atmosphere, to a mixture of 95 g of α-methylstyrene, 50 g of toluene, 0.5 g of polyethyleneglycol having a molecular weight of 12,000 and 0.5 g of polyhydroxyethylene cetylether, at 15° C, 0.5 g of sec.-butyllithium (15% solution in n-hexane) is added. After 2 minutes reaction time, to the reaction solution, which is already slightly viscous, 5 g of styrene dissolved in 100 g of toluene, are added. After 5, 10 and 15 minutes reaction time, at each time a further amount of 0.1 g of sec.-butyllithium is added. After a total reaction time of 1 hour, the reaction solution is diluted with benzene and the polymer is precipitated in methanol, to which some acetic acid is added. The polymer is dried at 100° C in vacuum.
Softening point:
185° C

K-value: 53.54

Composition of the polymer:

90.43% α-methylstyrene
9.57% styrene

Example 5

In a nitrogen atmosphere, to a mixture consisting of 95 g of styrene, 5 g of α-methylstyrene, 500 g of toluene and 1 g of polyethyleneglycol having a molecular weight of 12,000, at 10° C, 0.2 g of n-butyllithium (15% solution in hexane) is added. The reaction starts immediately and the temperature rises up to about 45° C. After 5 and 15 minutes reaction time, at each time 0.2 g of n-butyllithium and 100 g of toluene are added. After 1 hour reaction time, the reaction solution is diluted with benzene and the polymer is precipitated in methanol, to which some acetic acid has been added. The product is dried in vacuum at 100° C.
Softening point:
134° C

K-value: 68.67

Composition of the polymer:

3.6% α-methylstyrene
96.4% styrene

Example 6

In a nitrogen atmosphere, to a mixture consisting of 80 g of α-methylstyrene, 100 g of toluene and 1 g of hydroxyethylated triethanolamine, at 10° C, 0.5 g of n-butyllithium (15% solution in hexane) is added. The reaction starts immediately and the temperature rises to about 28° C. After 10 minutes 0.2 g of butyllithium is added. After 20 minutes, 20 g of methylethacrylate dissolved in 100 parts of toluene is added and after a further 10 minutes 0.2 g of butyllithium and 50 g of toluene are added. After a total reaction time of 1.5 hours, the solution is diluted and the polymer is precipitated in methanol. The polymer is dried at 100° C in vacuum.
Softening point:
190° C

K-value: 50.11

Composition of the polymer:

34.1% methylmethacrylate
65.9% α-methylstyrene

Example 7

In a nitrogen atmosphere, to a mixture consisting of 70 parts of α-methylstyrene, 50 g of toluene, 0.5 g of polyglycol having a molecular weight of 2,000 and 0.5 g of polyhydroxyethylene monostearate, at 10° C, 0.5 g of n-butyllithium are added. After 20 minutes 20 g of styrene dissolved in 200 g of toluene are added drop by drop in quick succession. After a total reaction time of 1.5 hours the reaction solution is diluted with benzene and the polymer is precipitated in methanol. The product is dried at 100° C in vacuum.
Softening point:
174° C

K-value 56.94

Composition of the polymer:

4.2% methylmethacrylate
23.9% styrene
71.9% α-methylstyrene

Example 8

In a nitrogen atmosphere, to a mixture consisting of 90 g of α-methylstyrene, 10 g of methylpentadiene-1,3, 100 g of toluene

and 1 g of polyhydroxyethylene cetylether, at 20° C 0.5 g of n-butyllithium (15% solution in hexane) are added. After 5 and 10 minutes reaction time further amounts to 0.1 g butyllithium and 50 g of toluene are at each time added. After one hour the reaction solution is diluted and the polymer is precipitated in methanol, to which some acetic acid is added. The product is dried at 100° C in vacuum.

Softening point:
182° C

K-value: 41.08

Composition of the polymer:

92.5% α-methylstyrene
7.5% methylpentadiene-1,3

Example 9

In a nitrogen atmosphere, to a mixture consisting of 80 g of α-methylstyrene, 20 g of 1-isopropyl-4-isopropenylbenzene, 50 g of toluene, and 1 g of polyhydroxyethylenesorbitan-monopalmitate, at 20° C, 0.5 g of n-butyllithium (15% solution in hexane) is added. After reaction times of 5 and 15 minutes 0.2 g of butyllithium and 50 g of toluene are added at each time. After 2 hours the reaction solution is diluted with benzene and the polymer is precipitated in methanol, to which some acetic acid has been added. The product is dried at 100° C in vacuum.

Softening point:
194° C

K-value: 40.44

Composition of the polymer:

86.5% α-methylstyrene
13.5% 1-isopropyl-4-isopropenylbenzene

Example 10

In the manner described in the above Example 1, 100 g of toluene, 125 g of α-methylstyrene, 0.6 g of polyhydroxyethylene cetylether and 0.6 g of hydroxyethylated β-naphthol, are mixed under nitrogen, cooled to −13° C and about 5 g of butadiene are introduced into said mixture. During the subsequent reaction butadiene is further introduced into the reaction solution. After the addition of 0.5 g of butyllithium (15% solution in hexane) the solution is deep yellow. The reaction starts slowly and the temperature rises to about −10° C. A further amount of 0.25 g of butyllithium is then added. At rising temperature, the solution becomes more viscous. At 35° C which is attained in about 30 minutes, the solution is deep red and very viscous. 75 g of toluene are now added. After 20 minutes, 0.1 g of butyllithium is added and introduction of butadiene is terminated. After a total reaction time of 90 minutes the viscous solution is diluted with benzene and the polymer is precipitated in methanol. The product is dried at 100° C in vacuum.

Softening point:
165° C

K-value: 57.60

Composition of the polymer:

91.0% α-methylstyrene
9.0% butadiene

Example 11

In a reaction vessel provided with stirrer, 500 g of toluene, 1.0 g of polyhydroxyethylene cetylether and 1.2 g of butyllithium (15% solution in hexane) are mixed under vacuum and at 15° C 100 g of α-methylstyrene are added. The reaction starts at once with strong discoloration of the solution. Simultaneously the reaction vessel is cooled in a cooling bath to −40° C within 30 minutes and kept at this temperature for 60 additional minutes. After a total reaction time of 1.5 hours, the very viscous solution is diluted, the polymer is precipitated in methanol and dried in vacuum at 100 to 120° C. 77 g of a colorless product are obtained.

Softening point:
208° C

K-value: 74.66

Example 12

In the manner described in Example 7, in a nitrogen atmosphere 350 g of toluene, 1 g of polyhydroxyethylene cetylether and 0.5 g of n-butyllithium (15% solution in hexane) are mixed and at 15° C 20 parts of a solution consisting of 90 g of α-methylstyrene and 10 g of styrene, dissolved in 150 g of toluene are added. After a short time the solution becomes deep red and is then cooled to −18° C while the rest of the monomer solution is slowly and constantly added drop by drop at this temperature. After 1.5 hours, the reaction solution is diluted, the polymer is precipitated in methanol and dried at 100° C in vacuum. 83 g of a colorless product are obtained.

Softening point:
174° C

K-value: 73.0

Composition of the polymer:

89.0% α-methylstyrene
11.0% styrene

Example 13

In the manner described in the above Example 1, in a nitrogen atmosphere 300 g of toluene, 90 g of α-methylstyrene and 1 g of polyhydroxyethyl stearate are mixed and at 15° C 0.6 g of n-butyllithum (15% solution in hexane) is added. After start of the reaction, the reaction solution is cooled to −15° C. After 30 minutes 10 g of methylpentadiene dissolved in 50 g of toluene are slowly added. After a total reaction time of

1.5 hours the reaction solution is diluted, the polymer is precipitated in methanol and dried at 100° C in vacuum. 67 g of a colorless product are obtained.

Softening point:
180° C

K-value: 45.0

Composition of the polymer:

94% of α-methylstyrene
6% of methylpentadiene

Example 14

In the manner described in the above Example 1, in a nitrogen atmosphere 300 g of toluene, 1 g of polyglycol having a molecular weight of 6,000 and 90 g of α-methylstyrene are mixed and at 15° C 0.6 g of n-butyllithium (15% solution in hexane) is added. After the start of the reaction the reaction solution is cooled to −30° C. After 1 hour, 10 g of methacrylic acid methylester dissolved in 25 g of toluene are slowly added drop by drop. Subsequently an additional amount of 0.2 g of n-butyllithium is added to the reaction solution. After a total reaction time of 2 hours, the viscous solution is diluted, the polymer is precipitated in methanol and dried at 100° C in vacuum. 62.1 g of a colorless product are obtained.

Softening point:
208° C

K-value: 62.23

Composition of the polymer:

87.7% α-methylstyrene
12.3% methacrylic acid methylester

Example 15

In the manner described in the above Example 1, 150 g of toluene, 1 g of polyhydroxyethylene cetylether and 0.7 g of n-butyllithium (15% solution in hexane) are mixed to a solution in a nitrogen atmosphere. At 15° C the addition, drop by drop, of a solution consisting of 25 g of diisopropenylbenzene and 100 g of toluene, is started. After formation of a colored complex, under constant addition drop by drop, the reaction solution is cooled to −18° C and the rest of the solution is added drop by drop. 15 minutes after terminating the addition, a solution consisting of 25 g of α-methylstyrene and 25 g of toluene is slowly added. After a total reaction time of 2 hours, the solution is diluted, the polymer is precipitated in methanol and dried at 40° C in vacuum. 31 g of a colorless product are obtained.

Softening point:
198°

K-value: 54.0

Composition of the polymer:

67.0% diisopropenylbenzene
33.0% α-methylstyrene

Example 16

Into a dry reaction vessel rinsed with nitrogen to a mixture of 200 g of α-methylstyrene, 0.25 g of polyhydroxyethylene cetylether, and 0.25 g of polyhydroxyethylene monostearate, at 15° C 0.25 g of n-butyllithium (20% solution in hexane) are added. The temperature in the reaction vessel rises at the start of polymerization to 35° C and decreases during a reaction time of 4 hours again to room temperature. 185 g of a clear, colorless product are obtained.

Softening point:
195° C

K-value: 79.5

Example 17

In the manner described in Example 16, to a mixture of 180 g of α-methylstyrene and 0.5 g of polyhydroxyethylene cetylether, at 15° C 0.25 g of butyllithium (20% solution in hexane) is added. The temperature in the reaction vessel increases at the start of polymerization to 35° C and decreases to room temperature in the course of the reaction time of 4 hours. 190 g of a clear, colorless product are obtained.

Softening point:
175° C

K-value: 78.3

Composition of the polymer:

89.6% of α-methylstyrene
10.4% of styrene

Example 18

In the manner described in the above Example 1, in a nitrogen atmosphere, 500 g of toluene, 0.5 g of polyhydroxyethylene cetylether, 0.5 g of hydroxybutylated hydroquinone and 1.2 g of n-butyllithium (15% solution in hexane) are mixed and at 15° C 100 g of α-methylstyrene are added. The reaction starts at once with strong discoloration of the solution. Simultaneously the reaction vessel is cooled in a cooling bath within 30 minutes to −40° C and kept at this temperature for 60 additional minutes. After a total reaction time of 1.5 hours the very viscus solution is diluted, the polymer is precipitated in methanol and dried at 100 to 120° C in vacuum. 77 g of a colorless product are obtained.

Softening point:
208° C

K-value: 74.66

The amount of the solvent used in carrying out the invention is in the range of 0 to 600% by weight based on the weight of monomers to be polymerized. After polymerization, the polymerizate is introduced

into and precipitated in 100 to 700% by weight of (based on the weight of the polymerizate) a lower alcohol, preferably methanol, to which 0.1 to 0.2% by weight of glacial acetic acid is added. The mol weights of the polymerizates obtainable according to this invention are in the range between 20,000 and 200,000.

WHAT WE CLAIM IS:—

1. Process for preparing homopolymerizates of α-methylstyrene and copolymerizates of α-methylstyrene with other ethylenically unsaturated monomers characterized in that the polymerization is carried out in the presence of both organometallic compounds of lithium, in the range fo 3 to 20 milli mols per mol of monomer, and a polymerization accelerator comprising a polyglycol of the formula

$$HOCH_3\ (—CH_2—O—CH_2)_n\ CH_2OH$$

wherein n has a value of from 5 to 200, the accelerator being present in an amount of from 0.5 to 2.0%, calculated on the weight of the monomers to be polymerized and the polymerization is carried out at a temperature of from −60° to + 60°C.

2. Process as claimed in claim 1, in which polymerization is started at a temperature above +10°C and is completed at temperatures below +10°C.

3. Process as claimed in claim 1 or 2, in which the polyglycol used is etherified with a compound selected from monohydric aliphatic alcohols, polyhydric aliphatic alcohols and amino alcohols.

4. Process as claimed in claim 1 or 2 in which the polyglycol used is esterified with organic acids.

5. Process as claimed in any preceding claim, in which a mixture of several accelerators is used.

6. Process as claimed in any preceding claim, in which polyglycols are used in admixture with hydroxyalkylated phenols.

7. Process for preparing homopolymerizates and copolymerizates of α-methylstyrene substantially as hereinbefore descriebd with reference to the Example given.

8. Homopolymerizates and copolymerizates of α-methylstyrene when prepared by a process as claimed in any preceding claim.

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